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(54) Title: NOVEL COMPOUNDS

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(57) Abstract: An adjuvant suitable for use with a lipophilic agrochemical has the formula (I), R₁-(CO)_m-O-[-R₂O-]_n-R₃, wherein R₁ is a C₁₆ to C₂₀ straight or branched chain alkyl or alkenyl group, R₂ is ethyl or isopropyl, n is from 8 to 30 and m is 0 or 1 and when R₂ is ethyl, R₃ is a C₁ to C₇ alkyl group and when R₂ is isopropyl, R₃ is hydrogen or a C₁ to C₇ alkyl group, provided that when R₁ is oleyl, R₂ is isopropyl and R₃ is hydrogen, n is not 10. An adjuvant composition comprising an agrochemical and an adjuvant of formula (I) is also claimed. Adjuvants of the invention show effective bioperformance enhancement despite having little or no surfactant properties.

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NOVEL COMPOUNDS

This invention relates to novel compounds and in particular to novel adjuvants and to their use in agrochemical formulations.

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A wide variety of adjuvants are available to those skilled in the art for the improvement of the bioperformance of active ingredients such as agrochemicals. In addition to the effect on bioperformance, the physical properties of an adjuvant are of key importance and must be selected with a view to compatibility with the formulation concerned. Thus by way of a single example, it is generally simpler to incorporate a solid adjuvant into a solid formulation such as a water-soluble or water-dispersible granule. In general adjuvants rely on surfactant properties for bioperformance enhancement and one typical class of adjuvants involves an alkyl or aryl group to provide a lipophilic moiety and a (poly) ethoxy chain to provide a hydrophilic moiety. Much has been published on the selection of adjuvants for various purposes and in Hess, F.D. and Foy, C.L., Weed technology, 2000, 14, 807-813 for example it is disclosed that adjuvants for use with lipophilic agrochemical active ingredients are generally of relatively low molecular weight with a degree of ethoxylation which leads to a hydrophile lipophile balance (HLB) of 8 or less. This corresponds to a surfactant with 12 carbon atoms in the lipophilic chain and between 2 and 3 moles of ethoxylate in the hydrophilic portion of the adjuvant. Similarly a surfactant with a longer carbon chain, such as 18 atoms, would have four or less moles of ethoxylate.

Propoxylate groups are considered to be lipophilic. A molecule with a hydrocarbon chain and propoxylate groups would not be considered to have an HLB value and would normally not be considered as a surfactant.

Particular care is required when selecting bioperformance enhancing adjuvants for incorporation in a microencapsulated presentation of an active ingredient, since many conventional ethoxylated adjuvants interfere with the microcapsule wall-forming reaction at the oil/water interface. Use of such adjuvants results in weak or ruptured microcapsules and their presence is therefore undesirable.

In GB 2024626 there is disclosed a range of polypropylene glycol derivatives suitable for destroying mites or ectoparasites and their eggs. In Table 3 there is disclosed propoxylated (10) oleyl alcohol.

We have now found that certain novel alkoxylated long-chain alcohols and acids and end-capped variants thereof, despite having little or no surfactant properties, are

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unexpectedly effective bioperformance enhancing adjuvants and furthermore have physical properties and attributes that render then particularly effective in certain formulation vehicles.

According to the present invention there is provided an adjuvant having the formula (I)

$$R_{1}$$
- (CO)_m - O - [- R_{2} O-]_n - R_{3} (I)

wherein R_1 is a C_{16} to C_{20} straight or branched chain alkyl or alkenyl group, R_2 is ethyl or isopropyl, n is from 8 to 30 and m is 0 or 1 and when R_2 is ethyl, R_3 is a C_1 to C_7 alkyl group and when R_2 is isopropyl, R_3 is hydrogen or a C_1 to C_7 alkyl group, provided that when R_1 is oleyl, R_2 is isopropyl and R_3 is hydrogen, n is not 10.

According to a further aspect of the present invention there is provided an agrochemical composition comprising a herbicide or fungicide and an adjuvant having the formula (I)

$$R_1$$
- (CO)_m - O - [- R_2 O-]_n - R_3 (I)

wherein R_1 is a C_{16} to C_{20} straight or branched chain alkyl or alkenyl group, R_2 is ethyl or isopropyl, n is from 8 to 30 and m is 0 or 1 and when R_2 is ethyl, R_3 is a C_1 to C_7 alkyl group and when R_2 is isopropyl, R_3 is hydrogen or a C_1 to C_7 alkyl group.

The agrochemical is preferably a lipophilic herbicide or fungicide...

When R_1 is an alkenyl group it may have one or more double bonds which may be in either cis or trans configuration(s). Preferably R_1 has from 1 to 3 double bonds. It is generally preferred that the double bond(s) are in the cis configuration. It is especially preferred that R_1 is a C_{18} branched chain alkyl or C_{18} alkenyl group for example oleyl or isostearyl (derived from the alcohol, 2-hexyl-dodecan-1-ol).

The value of n is preferably from 10 to 30 and especially from 10 to 20. The value of n may be an integer when a specific and uniform number of groups R_2O are introduced or may be an average value when a range of numbers of such groups are introduced.

The value of m is preferably 0.

When R_3 is not hydrogen it is preferably a C_1 to C_4 alkyl group and in particular methyl or butyl. Butyl is especially preferred. Those skilled in the art will appreciate that an alkyl group R_3 represents an "end cap" to the terminal hydroxyl of the group

$$-O-[-R_2O-]_n-H.$$

Since "end capping" a terminal ethylene oxide group (R₂ is ethyl) removes certain undesirable properties (such as the interference with the microencapsulation process) as

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discussed herein, it is desirable in order to achieve the objects of the invention to "end cap" substantially all of the terminal hydroxyl groups when R_2 is ethyl. Thus R_3 is not hydrogen when R_2 is ethyl. When R_2 is isopropyl on the other hand, R_3 may be hydrogen or alkyl since both moieties achieve the objects of the invention. It is thus possible to "end cap" only a proportion of the terminal hydroxyl groups such that R_3 is a mixture of hydrogen and alkyl groups.

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We have found that both propoxylated oleyl and isostearyl alcohols (when the value of m is 0) and acids (when the value of m is 1) and their end-capped equivalents show no significant surfactant properties. These materials do not contain a hydrophilic moiety and would not be considered to have an HLB classification. Attempts to use these materials to emulsify a simple oil such as decane into water showed that separation into two phases occurred even after vigorous shaking. Where some small amount of emulsification was observed this was found to be short lived. . Surprisingly the bioperformance enhancement, in particular for lipophilic agrochemicals, is excellent despite the lack of surfactant properties. Moreover, the absence of surfactant properties may bring a number of advantages such as reduced spray drift, a reduction in adverse interaction with surfactants added for formulation purposes (such as suspension of a dispersed solid) and reduced gelling of the formulation. Moreover the adjuvants are generally liquids (oils) which are substantially insoluble in water and are readily compatible for example with emulsion concentrates in which they dissolve in the oil phase. They are also more readily used as stand-alone tank mix adjuvants since they are oil-soluble. Increasing the molecular weight, for example using butyl end-capping and a value of n towards the upper end of the range, may produce a solid adjuvant which is for example well adapted for incorporation in solid formulations such as water-soluble or water-dispersible granules. In general the propoxylated adjuvants of the present invention are liquid whereas the ethoxylates are either solid or semi-solid. An exception is oleyl 10 EO with a butyl end cap which is a liquid.

We have found similarly that ethoxylated oleyl and isostearyl end-capped methyl and butyl ethers show no significant surfactant properties. They generally have different physical properties from the uncapped equivalents which can be used to advantage. For example oleyl 10 EO end-capped butyl ether is an oily liquid which emulsifies readily in water whilst the uncapped oleyl 10 EO equivalent forms viscous liquid crystals on contact with water. Increasing the molecular weight, for example using butyl end-capping and a value of n towards the upper end of the range, may produce a solid adjuvant which is for

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example well adapted for incorporation in solid formulations such as water-soluble or water-dispersible granules. Typical of such a solid adjuvant according to the present invention is oleyl 20 EO end-capped with butyl (i.e. the compound in which R_1 is oleyl, R_2 is ethyl, n is 20 and R_3 is butyl).

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As specific examples of the adjuvants of the present invention or which may be used in agrochemcial compositions of the present invention there may be mentioned oleyl 10 propylene oxide (i.e. a compound of Formula (1) wherein R1 is oleyl, m is 0, R_2 is isopropylene, n is 10 and R_3 is hydrogen), oleyl 10 propylene oxide end-capped butyl ether (i.e. a compound of Formula (1) wherein R1 is oleyl, m is 0, R_2 is isopropylene, n is 10 and R_3 is butyl), oleyl 20 propylene oxide, oleyl 20 propylene oxide end-capped butyl ether, isostearyl 10 propylene oxide, isostearyl 20 propylene oxide, oleyl 10 ethylene oxide end-capped butyl ether, oleic acid 10 ethylene oxide end-capped methyl ether (i.e. a compound of Formula (1) wherein R1 is oleyl, m is 1, R_2 is ethylene, n is 10 and R_3 is methyl), oleic acid 20 ethylene oxide end-capped methyl ether.

Adjuvants of the present invention are generally compatible with microencapsulation processes and can be incorporated as bioperformance enhancing adjuvant in a microencapsulated agrochemical formulation without detriment to the microcapsule properties. In contrast conventional ethoxylated alcohol surfactants tend to interfere with interfacial polymerisation wall-forming processes which are key to most conventional microencapsulation processes.

Adjuvants of the present invention have a variety of uses but are particularly suitable for enhancing the bioperformance of lipophilic agrochemicals, including herbicides, fungicides and insecticides. Examples of suitable lypophilic agrochemicals include herbicides such as fluzifop, mesotrione, fomesafen, tralkoxydim, napropamide, amitraz, propanil, cyprodanil, pyrimethanil, dicloran, tecnazene, toclofos methyl, flamprop M, 2,4-D, MCPA, mecoprop, clodinafop-propargyl, cyhalofop-butyl, diclofop methyl, haloxyfop, quizalofop-P, indol-3-ylacetic acid, 1-naphthylacetic acid, isoxaben, tebutam, chlorthal dimethyl, benomyl, benfuresate, dicamba, dichlobenil, benazolin, triazoxide, fluazuron, teflubenzuron, phenmedipham, acetochlor, alachlor, metolachlor, pretilachlor, thenylchlor, alloxydim, butroxydim, clethodim, cyclodim, sethoxydim, tepraloxydim, pendimethalin, dinoterb, bifenox, oxyfluorfen, acifluorfen, fluoroglycofen-ethyl, bromoxynil, ioxynil, imazamethabenz-methyl, imazapyr, imazaquin, imazethapyr, imazapic, imazamox,

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flumioxazin, flumiclorac-pentyl, picloram, amodosulfuron, chlorsulfuron, nicosulfuron, rimsulfuron, triasulfuron, triallate, pebulate, prosulfocarb, molinate, atrazine, simazine, cyanazine, ametryn, prometryn, terbuthylazine, terbutryn, sulcotrione, isoproturon, linuron, fenuron, chlorotoluron, metoxuron, 8-(2,6-diethyl-4-methyl-phenyl)tetrahydropyrazolo[1,2d][1,4,5]oxadiazepine-7,9-dione and 2,2,-dimethyl-propionic acid-8-(2,6-diethyl-4-methylphenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepine-7-yl ester, fungicides such as azoxystrobin, trifloxystrobin, kresoxim methyl, famoxadone, metominostrobin, picoxystrobin, dimoxystrobin, fluoxastrobin, orysastrobin, metominostrobin, prothioconazole, carbendazim, thiabendazole, dimethomorph, vinclozolin, iprodione, dithiocarbamate, imazalil, prochloraz, fluquinconazole, epoxiconazole, flutriafol, azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, hexaconazole, paclobutrazole, propiconazole, tebuconazole, triadimefon, trtiticonazole, fenpropimorph, tridemorph, fenpropidin, mancozeb, metiram, chlorothalonil, thiram, ziram, captafol, captan, folpet, fluazinam, flutolanil, carboxin, metalaxyl, bupirimate, ethirimol, and insecticides such as thiamethoxam, imidacloprid, acetamiprid, clothianidin, dinotefuran, nitenpyram, fipronil, abamectin, emamectin, bendiocarb, carbaryl, fenoxycarb, isoprocarb, pirimicarb, propoxur, xylylcarb, asulam, chlorpropham, endosulfan, heptachlor, tebufenozide, bensultap, diethofencarb, pirimiphos methyl, aldicarb, methomyl, cyprmethrin, bioallethrin, deltamethrin, lambda cyhalothrin, cyhalothrin, cyfluthrin, fenvalerate, imiprothrin, permethrin, halfenprox.

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Adjuvants of the present invention may be prepared by conventional techniques. Thus for example the ethoxylated or propopoxylated alcohol or acid may be manufactured by base catalysed condensation of the relevant alcohol or acid (for example oleyl or isostearyl alcohol or acid) with ethylene oxide (or propylene oxide as the case may be). End-capped derivatives may be obtained by reacting the ethoxylated or propoxylated alcohol or acid with the appropriate alkyl halide (for example butyl chloride) in the presence of a base.

The proportion of adjuvant relative to active ingredient can readily be selected by one skilled in the art to meet the intended utility. Typically the ratio of adjuvant to active ingredient will range from 1:50 and 200:1 and preferably from 1:5 to 20:1

The invention is illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

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EXAMPLES 1 to 10

Compounds of the present invention or for use in agrochemical compositions of the present invention are characterised as indicated below. In each case NMR spectra were run as 10 % v/v solutions in CDC13 on a Varian Inova 400 spectrometer. A bold and underlined

5 hydrogen indicates the hydrogen responsible for the relevant signal.

Oleyl 10 propylene oxide

	δ5.34	multiplet		2H	oleyl 9 & 10CH
	δ4 - 3	multiplet		32H	oleyl 1CH ₂ & propoxyl 1CH ₂ & 2CH
	δ2.01	multiplet		4H	oleyl 8 & 11CH₂
10	δ1.56	multiplet		2H	oleyl 2CH₂
	δ1.26	mutliplet		22H	oleyl 3 - 7 & 12 - 17CH ₂
	δ1.14	multiplet		30H	propoxylate 3CH ₃
	δ0.88	triplet	J≈6.9Hz	3H	oleyl 18CH ₃

Oleyl 10 propylene oxide end-capped butyl ether

15	δ5.34	multiplet		2H	oleyl 9 & 10CH
		multiplet		34H	butyl 1CH ₂ , oleyl 1CH ₂ & propoxyl 1CH ₂ &
	2CH				
	δ2.02	multiplet		4H	oleyl 8 & 11CH ₂
	δ1.55	multiplet		4H	oleyl 2CH ₂ & butyl 2CH ₂
20	δ1.35	sextuplet		2H	butyl 3CH ₂
	δ1.26	mutliplet		22H	oleyl 3 - 7 & 12 - 17CH ₂
	δ1.14	multiplet		30H	propoxylate 3CH ₃
	δ0.92	triplet	J≈7.3Hz	3H	butyl 4CH ₃
	δ0.88	triplet	J≈7.0Hz	3H	oleyl 18CH ₃

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Oleyl 20 propylene oxide

	δ5.34	multiplet		2H	oleyl 9 & 10CH
	δ4 - 3	multiplet		62H	oleyl 1CH ₂ & propoxyl 1CH ₂ & 2CH
	$\delta 2.01$	multiplet		4H	oleyl 8 & 11CH ₂
30	δ1.56	multiplet		2H	oleyl 2CH₂
	δ1.26	mutliplet		22H	oleyl 3 - 7 & 12 - 17CH ₂
	δ1.14	multiplet		60H	propoxylate 3CH₃
	δ0.88	triplet	J≈6.9Hz	3H	oleyl 18CH ₃

35 Oleyl 20 propylene oxide end-capped butyl ether

	δ5.34	multiplet	2H	oleyl 9 & 10CH
	δ4 - 3	multiplet	64H	butyl 1CH ₂ , oleyl 1CH ₂ & propoxyl 1CH ₂ & 2CH
	δ2.02	multiplet	4H	oleyl 8 & 11CH ₂
40	δ1.55	multiplet	4H	oleyl 2CH ₂ & butyl 2CH ₂
	δ1.35	sextuplet	2H	butyl 3CH₂

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		δι 26	mutliplet		22H	oleyl 3 - 7 & 12 - 17CH ₂
			multiplet		60H	propoxylate 3CH ₃
			triplet	J≈7.3Hz	3H	butyl 4CH ₃
			triplet	J≈7.0Hz	3H	oleyl 18CH ₃
		00.88	прієї	J≈7.UMZ	ЭП	oleyi 16Cn ₃
	5	Isoste	aryl (2-hex	<u>cyl-dodeca</u>	<u>n-1-ol) 10 p</u>	ropylene oxide
		δ4 - 3	multiplet		32H	dodecyl 1CH ₂ & propoxyl 1CH ₂ & 2CH
		δ1.56	multiplet		2H	dodecyl 2CH ₂
		δ1.26	mutliplet		27H	dodecyl 3 - $11CH_2$, 6CH & hexyl $1 - 5CH_2$
		δ1.14	multiplet		30H	propoxylate 3CH ₃
	10	δ0.88	triplet	J≈6.9Hz	3H	decyl 12CH ₃ & hexyl 6CH ₃
		Isoste	aryl (2-hez	<u>xyl-dodeca</u>	n-1-ol) 20 p	ropylene oxide
		δ4 - 3	multiplet		62H	dodecyl 1CH ₂ & propoxyl 1CH ₂ & 2CH
			multiplet	•	2H	dodecyl 2CH ₂
			mutliplet		27H	dodecyl 3 - 11CH ₂ , 6CH & hexyl 1 - 5CH ₂
	15		multiplet		60H	propoxylate 3CH ₃
			triplet	J≈6.9Hz	3H	decyl 12CH ₃ & hexyl 6CH ₃
		<u>Oleyl</u>	10 ethylen	e oxide en	d-capped b	utyl ether
		გ5 35	multiplet		2H	oleyl 9 & 10CH
		δ3.65	-		32H	polyethoxyl mid chain CH ₂
	20		multiplet		4H	polyethoxyl –OC <u>H</u> ₂ CH ₂ OR
,	20		multiplet		4H	polyethoxyl –OCH ₂ CH ₂ OR
			triplet	J≈6.5Hz	2H	butyl 1CH ₂
			triplet	J≈6.5Hz	2H	oleyl 1CH ₂
			•	J≈0.5∏Z	2H 4H	oleyl 8 & 11CH ₂
	0.5		multiplet		4H	oleyl 2CH ₂ & butyl 2CH ₂
	25		multiplet			- · · · · · · · · · · · · · · · · · · ·
			sextuplet		2H	butyl 3CH ₂
		δ1.26	•	T 7 0TT-	22H	oleyl 3 - 7 & 12 - 17CH ₂
		δ0.92	•	J≈7.3Hz	3H	butyl 4CH ₃
			triplet	J≈7.0Hz	3H	oleyl 18CH₃
	30	<u>Oleyl</u>	20 ethylen	<u>e oxide enc</u>	d-capped bi	utyl ether
			multiplet		2H	oleyl 9 & 10CH
		δ3.65	singlet		72H	polyethoxyl mid chain CH ₂
		δ3.63	multiplet		4 H	polyethoxyl -OC <u>H</u> 2CH2OR
		δ3.58	multiplet		4H	polyethoxyl -OCH2CH2OR
	35	δ3.46	triplet	J≈6.5Hz	2H	butyl 1CH ₂
		δ3.46	triplet	J≈6.5Hz	2H	oleyl 1CH ₂
		δ2.01	multiplet		4 H	oleyl 8 & 11CH ₂
		δ1.57	multiplet		4H	oleyl 2CH ₂ & butyl 2CH ₂
		δ1.35	sextuplet		2H	butyl 3CH ₂
	40	δ1.26	mutliplet		22H	oleyl 3 - 7 & 12 - 17CH ₂
		δ0.92	triplet	J≈7.3Hz	3H	butyl 4CH ₃
		δ0.88	triplet	J≈7.0Hz	3H	oleyl 18CH ₃

Oleic acid 10 ethylene oxide end-capped methyl ether

	0.010				
	δ5.33	multiplet		2H	oleoyl 9 & 10CH
	δ4.22	triplet	J≈4.9Hz	2H	polyethoxyl -OCH2CH2OC=O
	δ3.70	triplet	J≈4.9Hz	2H	polyethoxyl –OCH2CH2OC=O
5	δ3.65	singlet		34H	polyethoxyl mid chain CH ₂
	δ3.55	triplet	J≈4.9Hz	2H	polyethoxyl -OCH ₂ CH ₂ OCH ₃
	δ3.38	singlet		2H	-OCH₃
	δ2.33	triplet	J≈7.5Hz	2H	oleoyl 2CH ₂
	δ2.01	multiplet		4H	oleoyl 8 & 11CH ₂
10	δ1.62	multiplet		2H	oleyl 3CH ₂
	δ1.28	mutliplet		20H	oleyl 4 - 7 & 12 - 17CH ₂
	δ0.88	triplet	J≈7.0Hz	3H	oleyl 18CH₃
	Oleic :	acid 20 eth	ylene oxid	le end-ca	pped methyl ether
	δ5.33	multiplet		2H	oleoyl 9 & 10CH

	δ5.33	multiplet		2H	oleoyl 9 & 10CH
15	δ4.22	triplet	J≈4.9Hz	2H	polyethoxyl -OCH2CH2OC=O
	δ3.70	triplet	J≈4.9Hz	2H	polyethoxyl –OCH2CH2OC=O
	δ3.65	singlet		74H	polyethoxyl mid chain CH ₂
	δ3.55	triplet	J≈4.9Hz	2H	polyethoxyl -OCH ₂ CH ₂ OCH ₃
	δ3.38	singlet		2H	-OCH ₃
20	δ2.33	triplet	J≈7.5Hz	2H	oleoyl 2CH ₂
	δ2.01	multiplet		4H	oleoyl 8 & 11CH₂
	δ1.62	multiplet	*	2H	oleyl 3CH ₂
	δ1.28	mutliplet		20H	oleyl 4 - 7 & 12 - 17CH ₂
	δ0.88	triplet	J≈7.0Hz	3H	oleyl 18CH ₃

EXAMPLES 11 to 14

An agrochemical composition was prepared containing 0.2 % v/v of an adjuvant in a track sprayer containing fluazifop P butyl emulsified at one of four different concentrations. Weeds which had been grown to the 2.3 leaf stage were sprayed using volumes of 200 l/ha. Each sample was replicated three times. The following weed species were tested:-

30 AVEFA Avena fatua (wild oats)

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LOLRI Lolium rigidum (rye grass)

TRZAW Triticum aestivum (wheat)

SETVI Setaria viridis (green foxtails)

Activity was measured 21 days after treatment and was compared with a standard composition containing only fluazifop-p-butyl. The concentration required to provide 90% weed kill was calculated and is given in TABLE 1 below together with the mean ED90 across the species.

TABLE 1
ED90 Values (g/ha) for Adjuvants of the Invention with Fluazifop-p-butyl

Adjuvant	AVEFA	LOLRI	TRZAW	SETVI	Mean (g/ha)
Oleyl 20E Bu Ether	19.5	27.5	21.4	16.5	21.2
Oleic 10E Me Ether	16.7	34.8	28.4	15.8	23.9
Oleyl 10P Bu Ether	19.8	34.9	29.2	16.7	25.2
Oleyl 20P Bu Ether	23.4	48.6	32.2	19	30.8
No Adjuvant	36.7	81.9	66.6	45.8	57.8

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EXAMPLES 15 to 25

Further adjuvants of the present invention were tested for activity in combination with fluzifop-p-butyl. Activity (% weed kill) was measured 21 days after treatment and is given as a mean of 3 replicates and 4 rates of fluzifop-p-butyl. All adjuvants were applied at 0.2% v/v. The results are given in Table 2 in comparison with a corresponding composition containing no adjuvant.

TABLE 2
Mean Activity (%)

					Mean over
Adjuvant	TRZAW	SETVI	LOLRI	AVEFA	all species
No adjuvant	19.3	58.2	37.1	62.4	44
Isostearyl 20 PO	37.3	80.9	52.5	58	57
Oleyl 20 PO Bu ether	38.8	75.9	46	67.4	57
Oleyi 20 PO	53.3	80.4	36.3	70.6	60
Oleyl 20 EO Me ether	52.1	74.6	54.9	72.3	63
Isostearyl 10 PO	53.8	81.8	51.8	67.8	64
Oleyl 10 PO Bu ether	45.8	84.2	54.4	71.4	64
Oleyl 10 EO Me ether	56.1	78.4	56.2	71.3	66
Oleyl 10PO	54.3	84.6	55.9	72.6	67
Oleyl 10 EO Bu ether	56	85.6	56.5	73.3	68
Oleyl 20 EO Bu ether	59.3	78.1	68.8	76.1	71

EXAMPLES 26 and 27

The indicated adjuvants were evaluated in combination with a thin leaved grass herbicide 2,2,-dimethyl-propionic acid-8-(2,6-diethyl-4-methyl-phenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepine-7-yl ester. The weeds were sprayed at the

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growth stages shown in the table with pesticide emulsions using a track sprayer and volumes of 200 l/ha. The adjuvants were added at 5% v/v as tank mix additives. Each result is the average of two replicates.

Treatment	Rate gai/ha	ALOMY	APESV	AVEFA	LOLMU	PHAPA	Mean All
							Weeds
No Adjuvant	5	5	5	0	0	0	2
•	7.5	13	5	0	0	5	5
	10	23	3	0	25	3	11
0.5% Oleyl							
10PO	5	55	23	70	33	23	41
	7.5	70	89	96	60	98	83
	10	92	98	98	80	99	93
0.5% Oleyl 10EO butyl							
capped	5	53	53	89	91	93	76
	7.5	75	97	98	98	96	93
	10	88	98	99	93	99	95

5 APESV (Apera Spica-Venti)

PHAPA (Phalaris paradoxa)

EXAMPLE 28

This example demonstrates the improvement in the biological activity of the fungicide azoxystrobin when applied with one of the novel adjuvants in glasshouse tests. The results quoted are the mean percentage disease control from four replicates on barley inoculated with Puccinia recondita. Azoxystrobin was applied from the commercial formulation Quadris 25 SC which was diluted to the strengths shown in the table. The adjuvant was added as a 0.5 % v/v tank mix.

Azoxystrobin mgai/l	No adjuvant control	Oleyl 20E Butyl capped
2.5	10.5	90.5
1.25	1.8	82.7
0.625	2.3	66.5
0	0	5.9

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CLAIMS

1. An adjuvant having the formula (I)

$$R_1-(CO)_m-O-[-R_2O-]_n-R_3$$
 (I)

- wherein R₁ is a C₁₆ to C₂₀ straight or branched chain alkyl or alkenyl group, R₂ is ethyl or isopropyl, n is from 8 to 30 and m is 0 or 1 and when R₂ is ethyl, R₃ is a C₁ to C₇ alkyl group and when R₂ is isopropyl, R₃ is hydrogen or a C₁ to C₇ alkyl group, provided that when R₁ is oleyl, R₂ is isopropyl and R₃ is hydrogen, n is not 10.
- 2. An adjuvant according to claim 1 wherein R₁ is an alkenyl group having from 1 to 3 double bonds.
 - 3. An adjuvant according to claim 1 or 2 wherein R_1 is a C_{18} branched chain alkyl or C_{18} alkenyl group.
 - 4. An adjuvant according to claim 3 wherein R1 is oleyl or isostearyl
 - 5. An adjuvant according to any of the preceding claims wherein m is 0.
- 15 6. An adjuvant according to any of the preceding claims wherein n is from 10 to 20.
 - 7. An adjuvant according to any of the preceding claims wherein when R_2 is not hydrogen it is methyl or butyl.
 - 8. Oleyl 10 propylene oxide end-capped butyl ether, oleyl 20 propylene oxide, oleyl 20 propylene oxide end-capped butyl ether, isostearyl 10 propylene oxide, isostearyl 20 propylene oxide, oleyl 10 ethylene oxide end-capped butyl ether, oleyl 20 ethylene oxide end-capped butyl ether, oleic acid 10 ethylene oxide end-capped methyl ether, and oleic acid 20 ethylene oxide end-capped methyl ether.
 - An agrochemical composition comprising an adjuvant according to any of the preceding claims.
- 25 10. An agrochemical composition comprising a herbicide or fungicide and an adjuvant having the formula (I)

$$R_1$$
- (CO)_m - O - [- R_2 O-]_n - R_3 (I)

wherein R_1 is a C_{16} to C_{20} straight or branched chain alkyl or alkenyl group, R_2 is ethyl or isopropyl, n is from 8 to 30 and m is 0 or 1 and when R_2 is ethyl, R_3 is a C_1 to C_7 alkyl group and when R_2 is isopropyl, R_3 is hydrogen or a C_1 to C_7 alkyl group.

11. An agrochemical composition according to claim 10 or 11 being encapsulated in a microcapsule.

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12. An agrochemical composition according to any of claims 10 to 12 wherein the agrochemical is fluazifop-p-butyl, azoxystrobin or 2,2,-dimethyl-propionic acid-8-(2,6-diethyl-4-methyl-phenyl)-9-oxo-1,2,4,5-tetrahydro-9H-pyrazolo[1,2-d][1,4,5]oxadiazepine-7-yl ester.

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INTERNATIONAL SEARCH REPORT

Interr at Application No PCT/GB 02/03906

A. CLASSI IPC 7	FICATION OF SUBJECT MATTER A01N25/00 A01N25/30 A01N43/0	60 A01N25/14								
According to	According to International Patent Classification (IPC) or to both national classification and IPC									
<u> </u>	SEARCHED									
	Minimum documentation searched (classification system followed by classification symbols)									
Documental	Documentation searched other than minimum documentation to the extent that such documents are included. In the fields searched									
Electronic d	ata base consulted during the international search (name of data ba	se and, where practical, search terms used	J)							
EPO-In	ternal									
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT									
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Special call	egories of ched documents :	"T" later document published after the inte	rnational filing date							
'A' docume	nt defining the general state of the art which is not ered to be of particular relevance	or priority date and not in conflict with cited to understand the principle or the invention	the application but							
"E" earlier d	ocument but published on or after the international	"X" document of particular relevance; the o	laimed invention							
"L" docume which i	"L" document which may throw doubts on priority claim(s) or involve an inventive step when the document is taken alone which is cited to establish the publication date of another "Y" document of particular relevance; the claimed invention									
'O' docume	"O" document referring to an oral disclosure, use, exhibition or cannot be considered to involve an inventive step when the document is combined with one or more other such docu-									
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_	ctual completion of the international search	Date of mailing of the international sea								
22	2 October 2002	31/10/2002								
Name and m	ailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,	Authorized officer								
	Fax: (+31-70) 340-2016	Glomm, B								

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